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Electrochemistry and Spectroelectrochemistry of Substituted Tetrabenzotriazaporphine

By

Y.-H. Tse, A. Goel, M. Hu, A.B.P. Lever*, C.C. Leznoff and J.E. Van Lier

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Electrochemistry and Spectroelectrochemistry of Substituted Tetrabenzotriazaporphine

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Electrochemistry and Spectroelectrochemistry of Substituted Tetrabenzotriazaporphine

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Abstract

The spectral and electrochemical properties of tetrabenzo[5,10,15]triazaporphine (TBTAP) and their magnesium derivatives, having a long alkyl chain attached to the meso-carbon have been studied. Both metal-free and metallated species show typical metal-free phthalocyanine-like spectra. Two reduction and two oxidation redox couples have been observed. The cation, anion and dianion species of these porphyrin derivatives have been electrochemically generated and their electronic spectra are recorded.

Introduction

Tetrabenzo[5,10,15]triazaporphine (TBTAP) differs from phthalocyanine (Pc) by a methine group, instead of a nitrogen, at a meso position. These unsymmetrical porphyrin derivatives have received relatively less attention, than related macrocyclic compounds. During the early development of phthalocyanine chemistry (1,2) it was shown that reaction of methylmagnesium halide with phthalonitrile yields magnesium tetrabenzotriazaporphine (TBTAPMg). Recently, a variety of TBTAP derivatives (3), substituted at both benzo and meso positions, were prepared using a similar procedure. When substituted phthalonitriles are used, inseparable mixtures of regioisomers are obtained. However tetrabenzotriazaporphines derived from unsubstituted phthalonitrile and long chain alkylmagnesium halide gave only one isomer which was usually readily soluble in organic solvents. Variations in the alkyl chain length of the Grignard reagent can provide an interesting series of new TBTAP(C_n)M derivatives substituted at the meso position ((C_n) designates the length of the alkyl chain at the meso position). Unsymmetrical porphyrins have also been used in cancer photodynamic therapy (4). The TBTAP derivatives may provide higher stability and efficiency, in this application, compared with the generally less stable porphyrin nuclei.

This work reports the syntheses of a series of metal-free, TBTAP(C_n)H₂, and metallated, TBTAP(C_n)M, species with an alkyl chain at the meso-position. The electrochemical and spectro-electrochemical properties of some of these derivatives will also be reported.

III. Results

Experimental

Materials: Tetrabutylammonium perchlorate (TBAP; Kodak) was recrystallized from absolute ethanol and dried in a vacuum oven at 50°C for 2 days. 1,2-Dichlorobenzene (DCB, Aldrich) and N,N-dimethylformamide (DMF; Aldrich) were used as supplied. Argon gas (Linde) was purified by passage through heated copper filings for electrochemical measurement. Matheson high-purity argon was used to maintain inert atmosphere conditions for syntheses.

Methods: Differential pulse voltammetry was performed with a Princeton Applied Research (PAR) Model 174A polarographic analyzer. Cyclic voltammetry was performed with a Pine

Instrument RDE-3 potentiostat, and rotating disk electrode studies with a Pine Instruments PIR Rotator.

A conventional three electrode cell was used in electrochemical experiments. A platinum (Pt) disk described by the cross-sectional area of a 27-gauge wire, sealed in glass, was used as the working electrode, a Pt wire as the counter electrode, and a AgCl/Ag wire as the quasi-reference electrode. Potentials were referenced internally to the ferricinium/ferrocene (Fc^+/Fc) couple. For the rotating disc study, a Pt disk with an area of 0.44 cm^2 was used as working electrode.

Electronic spectra were recorded with a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyser or a Cary Model 2400 spectrometer. Spectroelectrochemical data were collected following a published design (5). Note we used an internal AgCl/Cl electrode and that in the thin layer cell, the actual potential of the AgCl/Ag electrode may deviate slightly from its true thermodynamic value. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs. Nuclear magnetic resonance (nmr) spectra were recorded on a Bruker AM300 nmr spectrometer. The observed splittings of the nmr signa's are described as singlets(s), doublets(d), triplets(t), or multiplets(m). Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

Thin-layer chromatography (tlc) was performed using silica gel G as the adsorbent. Flash chromatography was performed using silica gel of particle size 20-45 micron. All reactions were stirred with a magnetic stirrer. Sublimations were carried out generally at 300°C and 0.005 torr pressure. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Syntheses

(27-Pentyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) magnesium (1)

Hexylmagnesium chloride (8.0 mL of 2M solution in diethyl ether, 16 mmol) was added dropwise to a stirred suspension of phthalonitrile (2 g, 15.6 mmol) in dry diethyl ether (10 mL), under an argon atmosphere. The reaction mixture was stirred for 2h. at room temperature. During this time the reaction underwent a colour change from a purple to a reddish-brown. Ether was removed by passing a stream of argon through the reaction flask for 15 min. to obtain a brown

residue. This residue was dissolved in distilled quinoline (5 mL) and stirred at 185°C, under argon. After 2h., the reaction mixture underwent a colour change from reddish-brown to green, and a tlc analysis (THF-hexane (1:4) as eluant) of this mixture showed the presence of a blue compound, a green compound, and a very mobile purple intermediate. After 24h., the purple intermediate had disappeared and the reaction mixture constituted mainly a blue and a green pigment. The reaction mixture was cooled to room temperature and passed through a silica gel column and eluted with THF-hexane (1:9). This procedure removed an insoluble blue-black impurity and gave a green fraction. Evaporation of the solvent gave a green semi-solid. A solution of this solid was loaded on a silica gel column (flash) and eluted with THF-hexane (1:9) to obtain a green and then a blue fraction. The blue fraction proved to be the magnesium phthalocyanine (by comparison of the uv/vis spectrum with an authentic sample). The green fraction was evaporated to obtain a green solid. A solution of this solid was loaded on a gel permeation column (Bio-beads, SX-2, 200-400 mesh) and eluted with THF. This procedure removed a residual trace of yellow impurity. Crystallization from ether-hexane (1:9) gave green needles. After sublimation, under reduced pressure, the sublimate was found to be pure (1) (TBTAP(C₅)Mg) (182 mg, 8% yield), uv/vis (THF) peak max nm (log ε): 668(5.20), 647(5.00), 615(4.10), 593(4.21), 445(4.43), 400(4.70); ir (cm⁻¹): 2920, 2860, 1490, 1330, 1290, 1170, 1130, 1120, 1090, 720; ¹H nmr (pyridine-d₅) : 10.14(m, 2H), 9.80(m, 4H), 9.36(m, 2H), 8.20(m, 8H), 5.40(m, 2H), 2.85 (m, 2H), 2.10(m, 2H), 1.58(m, 2H), 1.01(t, J = 7.0 Hz, 3H)ppm; ms m/z: 605(M +, 100), 548(55), 274(28). Anal. calcd. for C₃₈H₂₇N₇Mg : C 75.32, H 4.49, N 16.18; found: C 75.28, H 4.72, N 16.01.

27-Pentyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine (2)

Species (1) (61 mg, 0.1 mmol) was dissolved in glacial acetic acid (10 mL), refluxed for 2h., cooled to room temperature, and centrifuged to obtain a bluish-green precipitate. The precipitate was washed with water and then with methanol. Reprecipitation from a concentrated solution of toluene by methanol gave a bluish-green solid. Crystallization from toluene gave bluish-green needles (44 mg, 75% yield). Residual traces of impurities were sublimed off, under reduced pressure, to obtain a pure sample of (2) (TBTAP(C₅)H₂), uv/vis (THF) peak max (log ε):

682(5.10), 642(4.89), 616(4.41), 589(3.79), 385(4.33); ir (cm^{-1}): 3440 (broad, NH), 2920, 2860, 1500, 1470, 1440, 1340, 1320, 1130, 1120, 1100, 1030, 760, 720; ms m/z: 583(M+, 100), 526(16); Anal. calcd. for $\text{C}_{38}\text{H}_{29}\text{N}_7$: C 78.19, H 5.01, N 16.80; found: C 78.00, H 4.77, N 16.60.

(27-Pentyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) zinc (3)

To a solution of (2) (29 mg, 0.05 mmol) in 5 mL of dry dimethylformamide(DMF)-toluene (1:1) was added anhydrous zinc acetate (92 mg, 0.5 mmol), and the mixture was refluxed for 20h. (under argon). The reaction mixture was cooled to room temperature and the solvent was evaporated to obtain a green solid. After washing with water and methanol, crystallization from ether gave crystals with a purple reflex. Impurities were removed by sublimation under reduced pressure, affording a residue of pure (3) (TBTAP(C_5)Zn) (26 mg, 80% yield) as microcrystals with a purple reflex, uv-vis (THF) peak max nm (log): 668(5.13), 645(4.98), 615(4.22), 591(4.21), 443(4.01), 385(4.50); ir (cm^{-1}): 2920, 2860, 1490, 1410, 1330, 1290, 1170, 1130, 1120, 1100, 780, 720; ms m/z: 645 (M+, 100), 588(39), 294(23). Anal. calcd. for $\text{C}_{38}\text{H}_{27}\text{N}_7\text{Zn}$: C 70.54, H 4.18, N 15.15; found: C 70.28, H 4.00, N 15.00.

(27-Nonyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) magnesium (4)

Decylmagnesium bromide (7.8 mL of 1 M solution in diethyl ether, 7.8 mmol) was added dropwise to a stirred suspension of phthalonitrile (1g, 7.8 mmol) in dry diethyl ether (5 mL), under an argon atmosphere. The reaction mixture was stirred for 2h. at room temperature. During this time, the reaction underwent a colour change from a purple to a reddish-brown. Ether was removed by passing a stream of argon through the reaction flask for 15 min. to obtain a brown residue which was dissolved in distilled quinoline (5 mL) and stirred at 120°C, under argon. After 2h., the reaction mixture underwent a colour change from reddish-brown to green, and a tlc analysis (pyridine-hexane (1:4) as eluant) of this mixture showed the presence of a blue compound, a green compound, and a very mobile purple intermediate. After 18h., the purple intermediate had disappeared and the reaction mixture constituted mainly a blue and a green pigment. The reaction mixture was cooled to room temperature and passed through a silica gel column and eluted with ether-hexane (1:1). This procedure removed an insoluble blue-black impurity and gave a green

fraction. Evaporation of the solvent gave a green semi-solid. A solution of this solid was loaded on a silica gel column (flash) and eluted with pyridine-hexane (1:4) to obtain a green and then a blue fraction. The green fraction was evaporated to obtain a green solid. Crystallization from ether-hexane (1:9) gave pure (**4**) (TBTAP(C₉)Mg) as green needles (100 mg, 8% yield), uv-vis (THF) peak max nm (log): 668(5.22), 647(5.06), 615(4.18), 593(4.25), 445(4.48), 400(4.74); ir (cm⁻¹): 2920, 2860, 1490, 1330, 1290, 1170, 1130, 1120, 1090, 720; ¹H nmr (pyridine-d₅) : 10.14 (m, 2H), 9.80 (m, 4H), 9.42 (d, J = 7.5 Hz, 2H), 8.22 (m, 8H), 5.46 (m, 2H), 2.92 (m, 2H), 2.22 (m, 2H), 1.62 (m, 2H), 1.60-1.20 (m, 8H), 0.91 (t, J = 7.0 Hz, 3H) ppm; ms m/z: 661(M +, 100), 548(41), 535(9).

27-Nonyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine (5)

Species (**4**) (75 mg, 0.11 mmol) was dissolved in glacial acetic acid (10 mL), refluxed for 2h., cooled to room temperature, and centrifuged to obtain a bluish-green precipitate. The precipitate was washed with water and then with methanol. Reprecipitation from a concentrated solution of toluene by methanol gave a bluish-green solid. Crystallization from toluene gave bluish-green needles (55 mg, 78% yield). Residual trace impurities were sublimed off, under reduced pressure, to obtain pure (**5**) (TBTAP(C₉)H₂), uv-vis (THF) peak max nm (log): 682(5.13), 642(4.93), 616(4.40), 589(3.80), 385(4.38); ir (cm⁻¹): 3440 (broad, NH), 2920, 2860, 1500, 1470, 1440, 1340, 1320, 1130, 1120, 1100, 1030, 760, 720; ms m/z: 639 (M +, 80), 473 (38); Anal. calcd. for C₄₂H₃₇N₇: C 78.85, H 5.83, N 15.32; Found: C 78.50, H 6.23, N 14.95.

(27-Nonyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) zinc (6)

To a solution of (**5**) (25.5 mg, 0.04 mmol) in 5 mL of dry dimethylformamide(DMF)-toluene (1:1) was added anhydrous zinc acetate (73.6 mg, 0.4 mmol), and the mixture was refluxed for 20h. (under argon). The reaction mixture was cooled to room temperature and the solvent was evaporated to obtain a green solid. After washing with water and methanol, crystallization from ether gave crystals with a purple reflex. Sublimation under reduced pressure afforded a sublimate of pure (**6**) (TBTAP(C₉)Zn) (24 mg, 85% yield) as microcrystals with a purple reflex, uv-vis (THF) peak max nm (log): 668(5.15), 645(4.98), 615(4.23), 591(4.20), 443(3.98), 385(4.58); ir (cm⁻¹): 2920,

2860, 1490, 1410, 1330, 1290, 1170, 1130, 1120, 1100, 780, 720; ms m/z: 703(M +, 71), 576(100), 471(34), 288(33).

(27-Tridecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) magnesium (7)

Tetradecylmagnesium chloride (7.8 mL of 1M solution in THF, 7.8 mmol) was added dropwise to a stirred suspension of phthalonitrile (1g, 7.8 mmol) in freshly distilled THF (5 mL), under an argon atmosphere. The reaction mixture turned purple immediately. The reaction mixture was stirred for a further 2h. at room temperature. During this time, the reaction underwent a colour change from a purple to a reddish-brown. Tetrahydrofuran was removed by passing a stream of argon through the reaction flask for 15 min. to obtain a dark brown residue which was dissolved in distilled quinoline (3 mL) and the mixture stirred at 120°C. under an argon atmosphere. After 0.5 h, the reaction mixture underwent a colour change from a reddish-brown to a dark green, and a tlc analysis (pyridine-hexane (1:4) as eluant) of this mixture showed the presence of a blue compound, a green compound, and a purple intermediate. After 18h the purple intermediate was still present. Hence, the temperature was raised to 180°C and the mixture was refluxed for a further 24h.. The reaction mixture was cooled to room temperature and the column was eluted with pyridine-hexane (1:4) and was evaporated to obtain a green oil. This oil was loaded on a short silica gel column (flash). The column was eluted with pyridine-hexane (1:4) and again eluted with pyridine-hexane (1:4). This chromatographic procedure afforded separation of the required product from the phthalocyanine by-product. The column was eluted with THF (1 mL) by methanol (9 mL) gave crude (¹TAP(C₁₃)Mg) (47 mg, 3% yield). After sublimation, under reduced pressure, the sublimate (7), uv-vis (THF) peak max nm (log ε): 668(5.25), 400(4.74); ir (cm⁻¹): 2920, 2860, 1490, 1330, 1290, 1170, 1130, 1120, 1090, 720; ¹H nmr (pyridine-d₅): 10.14 (m, 2H), 9.80 (m, 4H), 9.42 (d, J = 7.0 Hz, 2H), 2.22 (m, 2H), 1.64 (m, 2H), 1.42-1.25 (m, 16H); ¹³C nmr (CDCl₃): 100, 548(44), 535(18); Anal. calcd. for C₄₆H₇₂N₂O₂: C 76.93, H 6.03, N 13.65; found: C 76.74, H 6.22, N 13.44.

27-Tridecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine (8)

Species (7) (40 mg, 0.056 mmol) was dissolved in glacial acetic acid (5 mL), refluxed for 2 h, cooled to room temperature, and centrifuged to obtain a bluish-green precipitate. The precipitate was washed with water and then with methanol, until the washings were colourless. Reprecipitation from a concentrated solution of toluene by methanol gave a bluish-green solid. Crystallization from toluene gave needles with a purple reflex (28 mg, 72% yield). After sublimation under reduced pressure, the residue was found to be the pure (8) TBTAP($C_{13}H_2$), uv-vis (THF) peak max nm (log_e): 682(5.15), 642(4.94), 616(4.45), 589(3.82), 385(4.47); ir (cm^{-1}): 3440 (broad, NH), 2920, 2860, 1500, 1470, 1440, 1340, 1320, 1130, 1120, 1100, 1030, 760, 720; ms m/z: 695 (M⁺, 100), 526 (10); Anal. calcd. for $C_{46}H_{45}N_7$: C 79.39, H 6.52, N 14.09; found: C 79.42, H 6.34, N 14.39.

(27-Tridecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) zinc (9)

Anhydrous zinc acetate (73.6 mg, 0.4 mmol) was added to a solution of (8) (17.35 mg, 0.025 mmol) in 5 mL of dry DMF-toluene (1:1) and the mixture refluxed for 24 h (under argon). The reaction mixture was cooled to room temperature and the solvent evaporated to obtain a green solid. After washing with water and methanol, crystallization from ether gave dark blue crystals. After sublimation under reduced pressure, the residue was found to be the pure (9) TBTAP($C_{13}Zn$), (12 mg, 63% yield), uv-vis (THF) peak max nm (log_e): 668(5.13), 645(5.00), 615(4.28), 591(4.25), 443(4.21), 385(4.63); ir (cm^{-1}): 3440, 2860, 1490, 1410, 1330, 1290, 1170, 1130, 1120, 1100, 780, 720; ms m/z: 758(M⁺, 100), 588(45), 294(14).

(27-Heptadecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) magnesium (10)

Octadecylmagnesium chloride (7.8 mL of dropwise to a stirred suspension of phthalonitrile under an argon atmosphere. The reaction mixture Tetrahydrofuran was removed by passing a stream of quinoline (5 mL) was added and the mixture stirred at 140°C, under argon, for 18 h. A tlc analysis (THF-hexane (1:1) as eluant) showed a very mobile green spot for the required product along with some brown impurities. The reaction mixture was cooled to room temperature and

passed through a silica gel column and eluted with THF-hexane (1:1). This procedure removed an insoluble blue-black impurity and gave a green fraction. A tlc analysis (pyridine-hexane (1:4) as eluant) of this fraction showed a green spot (R_f 0.9) for the required magnesium tetrabenzotriazaporphine and a blue spot (R_f 0.25) for the magnesium phthalocyanine byproduct. The solvent was evaporated and the residue loaded onto a silica gel column (flash) and eluted with pyridine-hexane (1:9). This chromatographic procedure afforded separation of the required **10** (TBTAP(C_{17})Mg) from the phthalocyanine byproduct. Crystallization from THF-methanol (1:1) gave **(10)** as needles with a purple reflex (86 mg, 6% yield), uv-vis(THF) peak max nm (log ϵ): 668(5.24), 647(5.06), 615(4.09), 593(4.20), 445(4.60), 400(4.71); ir (cm^{-1}): 2920, 2860, 1490, 1330, 1290, 1170, 1130 1120, 1090, 720; 1H nmr (pyridine-d₅) :10.14(m, 2H), 9.8(m, 4H), 9.42(d, J = 7.9 Hz, 2H), 8.22(m, 2H), 5.46(m, 2H), 2.92(m, 2H), 2.21(m, 2H), 1.62(m, 2H), 1.42-1.23(m, 24H), 0.84(t, J = 7.0 Hz, 3H)ppm; ms m/z: 774(M +, 100), 548(56), 535(20).

27-Heptadecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine (11)

Compound **(10)** (86 mg, 0.11mmol) was dissolved in glacial acetic acid (5 mL), refluxed for 2h., cooled to room temperature, and centrifuged to obtain a bluish-green precipitate. The precipitate was washed with water and then with methanol until the washings were colourless. Reprecipitation from a concentrated solution of toluene by methanol gave a bluish-green solid. Crystallization from toluene gave plates with a purple reflex (60 mg, 70% yield). After sublimation under reduced pressure, the residue was found to be **pure (11)** TBTAP(C_{17})H₂, uv-vis (THF) peak max nm (log ϵ): 682(5.28), 642(5.09), 616(4.61), 445(3.71), 385(4.46); ir (cm^{-1}): 3260 (broad, NH), 2920, 2860, 1500, 1470, 1440, 1340, 1320, 1130; 1120, 1090, 1060, 1030, 760, 720; ms m/z: 751(M +, 100), 526(9)

(27-Heptadecyl-29H,31H-tetrabenzo[b,g,l,q][5,10,15]triazaporphine) zinc (12)

To a solution of **(11)** (30 mg, 0.04mmol) in 1mL of dry DMF-toluene (1:1) was added anhydrous zinc acetate (73.6 mg, 0.4 mmol), and the mixture was refluxed for 24h. (under argon). The reaction mixture was cooled to room temperature and the solvent evaporated to obtain a green solid. After washing with water and methanol, crystallization from ether gave a bluish-green solid.

Further purification by flash chromatography using a solvent system of pyridine-hexane (1:9) and sublimation under reduced pressure gave a residue with a purple reflex. It was found to be the pure (12) TBTAP(C₁₇)Zn (20 mg, 61% yield), uv-vis (THF) peak max nm (log ε): 668 (5.23), 645(5.05), 615(4.34), 591(4.29), 443(4.16), 385(4.66); ir (cm⁻¹): 2920, 2860, 1490, 1410, 1330, 1290, 1170, 1130, 1120, 1100, 780, 720; ms m/z: 814 (M +, 100), 589 (47), 575(29), 294 (21); Anal. calcd. for C₅₀H₅₁H₁₇Zn: C 73.65, H 6.30, N 12.02; found: C 73.60, H 6.43, N 12.55.

2,9,16,23-Tetrakis(2,2-dimethylethyl)-27-pentadecyl-29H,31H-tetrabenzo[b,g,l,q] [5,10,15] triazaporphine (TBuTBTAP(C₁₅)H₂) (13) and 2,11,20,29-tetrakis(2,2-dimethylethyl)-34-pentadecyl-37H,39H-tetranaphtho [2,3-b:2',3'-g:2'',3''-1-2'',3''-q] [5,10,15] triazaporphine (14) (t-NTNTAP(C₁₅)H₂) were synthesized as previously described (3).

Results and Discussion

A. Syntheses: Reaction of phthalonitrile with a variety of Grignard reagents led to the formation of magnesium tetrabenzotriazaporphines, TBTAP(C_n)Mg, along with some magnesium phthalocyanine (MgPc) by-product. Magnesium tetra- or triazaporphines could be separated from the magnesium phthalocyanine by using flash chromatography. Sometimes, it was necessary to filter the product mixture through a normal silica gel column to remove insoluble impurities, before performing the flash chromatography. Magnesium species were further purified by crystallization from ether-hexane or tetrahydrofuran (THF)-methanol, and sublimation under reduced pressure. The sublimate was usually a brownish residue, which was identified as TBTAP(C_n)Mg.

Magnesium tetrabenzotriazaporphines could be demetallated by refluxing in glacial acetic acid. Metal-free tetrabenzotriazaporphines (TBTAP(C_n)H₂) were generally less soluble than the corresponding magnesium tetrabenzotriazaporphines. Metal-free tetrabenzotriazaporphines were

purified by crystallization from toluene, followed by removal of impurities by sublimation, the residue after sublimation being the required TBTAP(C_n)H₂. Zinc tetrabenzotriazaporphines could be obtained from reaction of the corresponding metal-free tetrabenzotriazaporphines and anhydrous zinc acetate.

B. Electronic structure of the TBTAP system: Simple PcM species have D_{4h} symmetry, while demetallation leads to the PcH₂ species of D_{2h} symmetry. However, in contrast, in the TBTAP species, the metallated complexes at best have two-fold symmetry, while the free base species cannot exceed C_S; thus all orbital degeneracies are lifted, for both metallated and free base. The electronic structure of TBTAPC₁Mg has been discussed by Solovev et al.(6) using Gouterman's four-orbital model. For the metal-free and main-group metal derivatives, the HOMO-1, HOMO, LUMO and LUMO + 1 orbitals of the TBTAP(C_n) system are [b₁(π)]², [a₂(π)]² [b₂(π^*)]⁰ and [b₁(π^*)]⁰ respectively (with electron occupations noted). Thus the overall electronic structure parallels that of metal free phthalocyanine.

C. Electrochemistry

The electrochemical properties of phthalocyanine species are well known (7). The electrochemistry of these triazabenzo porphine species were briefly studied to investigate how the replacement of one aza bridgehead by a long-chain-linked CH methine bridgehead, influenced these properties.

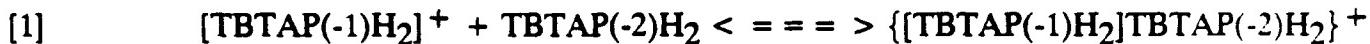
i) **TBTAP(C_n)H₂:** Species (5), n = 9, and (11), n = 17, were chosen to study the effect of the length of the alkyl group in the meso position on the electrochemical properties of the unsubstituted benzo TBTAP derivatives. The electrochemistry of species (13) and (14), n = 15, were investigated to monitor the effect of changing the substituents on the benzo position.

Oxidation and reduction of these compounds directly involve the triazaporphine ring system, since the metal centres are not redox active. Cyclic voltammograms generally show (e.g. Figure 1a) (Table I) three waves (2 reduction (III,IV), 1 oxidation (I) (III,IV are reversible or quasi-reversible, I is usually irreversible) diffusion controlled with $i_C = i_a$, and $i_O \propto v^{1/2}$ (v = scan rate in cyclic voltammogram), and in addition, two less well defined and overlapping oxidation waves, II and II'.

The rest potential lies between processes II' and III.

A rotating disc (RDE) analysis shows that the sum of the limiting current for waves II and II' corresponds to a one electron-transfer process (Figure 1b) and equal to the current for process I. Thus processes II and II' (combined) correspond with ring oxidation to the cation radical, $[TBTAP(-1)H_2]^+$ / $TBTAP(-2)H_2$ (using previously defined nomenclature (8)). A differential-pulse voltammetry study shows that the redox potentials for wave II and II' are concentration dependent. At very low concentration, only one differential-pulse signal was observed at a potential close to that of wave II' (Table I, Figure 2). The concentration limit for observing one peak for species (5) and (13) is below $10^{-5} M$, and is below $10^{-6} M$ for species (14).

The dual wave arises from aggregation, a well known phenomenon in phthalocyanine derivative chemistry (9). However Beer-Lambert-plots for the parent (5) from $8.2 \times 10^{-5} M$ to $6.6 \times 10^{-7} M$ at 687 and 647 nm do not show any deviation from linearity indicating that the parent un-oxidised species, is not aggregated. Therefore the oxidised species, $[TBTAP(-1)H_2]^+$ must aggregate according to:



Since it is apparently Wave II' and not Wave II which survives in very dilute solution, Wave II' must correspond to oxidation of the mononuclear species which then combines, as in [1] to form a mixed valence species which then oxidises at Wave II to 2 $[TBTAP(-1)H_2]^+$ (but see below that this species is in equilibrium with a dipositively charged dimeric species) The equilibrium [1] becomes much less important at very low concentrations as shown in Figure 2, when only direct oxidation of $TBTAP(-2)H_2$ to $[TBTAP(-1)H_2]^+$ is observed. The formation of binuclear mixed valence single ring oxidised species such as that shown in (1) is becoming fairly well known in phthalocyanine chemistry especially with binuclear linked species (10-12), but also purported to occur (13) during the oxidation of MgPc(-2), via $[MgPc(-1).MgPc(-2)]^+$ to 2 $[MgPc(-1)]^+$.

Wave I is assigned to oxidation to the dication radical, namely process $[TBTAP(0)H_2]^{2+}/[TBTAP(-1)H_2]^+$. This redox couple is irreversible except for species (14).

Waves III and IV are quasi-reversible diffusion-controlled one-electron transfer processes assigned to the reduction processes $\text{TBTAP}(-2)\text{H}_2$ / $[\text{TBTAP}(-3)\text{H}_2]^-$ and $[\text{TBTAP}(-3)\text{H}_2]^-$ / $[\text{TBTAP}(-4)\text{H}_2]^{2-}$ respectively.

Increasing the alkyl chain from 9 to 17 carbon atoms in the meso position, provides no significant change in the redox potential.

ii) $\text{TBTAP}(\text{C}_n)\text{Mg}$ (species 4, 10): These magnesium species show voltammograms typical for MPc-like species with oxidation processes II and I to the ring oxidised mono- and di-cation radical, respectively, and two reduction processes (III, IV) to the ring reduced mono-and di-anion radical respectively (Figures 3,4, Table I). The forward and reverse differential pulse polarograms are especially well behaved (Figure 4) showing the electrochemical reversibility of all the observed processes, with the exception of I (and possibly IV, see below).

iii) Comparison with regular phthalocyanine species: Although the overall features in the electrochemical behaviour of the TBTAP species parallel those of the phthalocyanines very closely, the first and second reductions for $\text{TBTAP}(\text{C}_n)\text{H}_2$ are about 300 mV negative of those for regular metal-free phthalocyanine species such as metal-free tetraneopentoxyphthalocyanine (6,14). This is due to the replacement of one electron withdrawing bridgehead nitrogen link, by the less withdrawing methine link. Porphyrins are more difficult to reduce than the corresponding phthalocyanines and these TBTAP species obviously lie, in character, in between the porphyrins and phthalocyanines.

The naphthalene substituted species, (14), is easier to oxidise and more difficult to reduce than the corresponding benzotriazaporphin, an observation consistent with previous phthalocyanine experience (7).

D. Electronic absorption

i) $\text{TBTAP}(\text{C}_n)\text{H}_2$ and $\text{TBTAP}(\text{C}_n)\text{M}$: In the electronic spectroscopy of four-fold symmetry, D_{4h} , MPc(-2) species, $\pi \rightarrow \pi^*$ transitions from the two upper filled π orbitals (HOMO, and HOMO-1) to the π^* LUMO orbital provide a strong band, usually in the range 620-720 nm, called the Q band and a second band, in the range 320 - 420 nm, called the B band (or Soret). The Q band is usually

$\pi_1 - \pi_1^*$

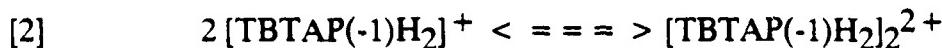
associated with a weaker vibrational satellite to higher energy (near 600 - 620 nm) (15). In the metal free species, of two-fold symmetry, the Q band is split into two strong features, usually with at least two weaker vibrational satellites. Such a doubled Q band is expected, and observed, in these lower symmetry TBTAP(-2)(C_n)H₂ and TBTAP(-2)(C_n)M species (Figure 5). The data reported here (Table II) correspond closely with those previously published for TBTAP(-2)H₂, TBTAP(-2)Mg and TBTAP(-2)Zn (3,5).

The Q band splitting in the spectra of the TBTAP(-2)(C_n)M species is about 500 cm⁻¹, whereas it is about 900 cm⁻¹ in the spectra of metal-free TBTAP(-2)(C_n)H₂, perhaps because of the lower symmetry of the latter. This Q band splitting is substantially larger than that imposed on mixed benzo, naphthophthalocyanines where one or three benzene rings is replaced by a naphthalene ring; such systems show splittings (16) of 225 - 250 cm⁻¹. Changing the length of the alkyl chain causes no significant shift, nor significant change in the relative intensities of either the Q or B bands, in the spectrum recorded in THF.

ii) Spectroelectrochemistry; a) Cation radicals, (a₂)¹, ²A₂: The spectroscopic changes accompanying the oxidation of TBTAP(C₉)Mg, (4) and t-BuTBTAP(C₁₅)H₂,(13), to their corresponding cation radicals are shown in Figures 6 and 7. The resulting loss of Q band intensity between 600 - 700 nm, and the growth of weaker and broader absorption near 550 and 850 nm, is typical of the formation of a phthalocyanine cation radical, Pc(-1), species (13,17,18) (Table III). Indeed the spectra (13,18) of ZnPc(-1) and MgPc(-1) species are dramatically similar to those spectra reported here, leaving no doubt that these species are cation radicals. The principal difference is that the band near 850 nm, reputed to be Q band for the monomeric cation radical (13) is relatively less strong, and is broader, than in the MPc(-1) species. The broadness may reflect incipient splitting in the lower symmetry of these species. The peak at 530 - 570 nm is a π-π transition in the mononuclear species, similar to previous assignments of related species (13,14,18,20,21).

These species show isosbestic points upon reduction and may be oxidised back to the starting species with recovery of the initial spectrum; thus the spectroelectrochemistry is reversible with no significant decomposition.

The presence of a hole in the HOMO orbital frequently leads, in phthalocyanine chemistry, to some stabilisation of a dimeric species (8,10-12,18,19) which may be written for the TBTAP species as:



Comparison of the electronic spectra of phthalocyanine and TBTAP cation radical spectra leads to the presumption that the peak at 1010 - 1080 nm arises from dimeric TBTAP radical cation species. Support for this conclusion arises from concentration dependent studies which show, for TBTAP(C₁₅)H₂, that the intensity ratio for the peak at 1070 nm relative to that at 860 nm, increases with increasing concentration e.g. the ratio 1070/860 is 0.4 at 2.5 x 10⁻⁴ M, and 1.1 at 1 x 10⁻³ M TBTAP(-2)H₂.

b) Mono-anion radicals (a₂)²(b₂)¹ 2B₂: Figure 8 shows the spectroscopic changes during the reduction of TBTAP(-2)(C₉)H₂, (5), to its anion radical, [TBTAP(-3)(C₉)H₂]⁻, with related data for other species in Table IV. Isosbestic points again attest to good behaviour with no significant decomposition. The spectroscopic features are characteristic of Pc(-3) anion radicals (14,16,22-24). While MPc(-2) species yield a single Q band, [MPc(-3)]⁻ species usually have a doubled band in the Q region. Conversely, these low symmetry [TBTAP(-3)(C_n)]⁻ species only exhibit a single band in the Q region (Figure 8). A magnetic circular dichroism study of these and related systems provides an explanation of this apparent anomaly and will be published elsewhere (25). Otherwise the spectra are characteristic of the mono-anion radical, especially with respect to the band near 440 nm and the double system (assigned as π^π - π^π) near 860 and 950 nm, which, however, is red shifted from the corresponding bands in the phthalocyanine series (14,22-24).

c) Di-anion radicals (a₂)²(b₂)² 1A₁: The spectroscopic changes during the reduction of the mono-anion radical of (13) to its di-anion radical are shown in Figure 9, with data for other di-anion radicals summarised in Table IV. The metal-free dianion radical spectra show clean complete reduction with isosbestic points. However, some decomposition is noted during the reduction of the Mg species to the di-anion state. These spectroscopic data are characteristic for Pc(-4) species.

especially the strong band near 530 nm;(14) in this case, the number of strong features in the $\text{Pc}(-4)$ and TBTAP(-4)(C_n) spectra and the overall shape of the band envelope are similar.

Summary The spectroscopic and electrochemical properties of the triazaporphine species parallel very closely those for two-fold symmetry metallophthalocyanines. The presence of one methine linkage replacing an aza bridgehead does not, it appears, have a major effect upon the electronic properties of these phthalocyanine-like species save for removing all orbital degeneracies. Thus the wealth of understanding which has grown in the phthalocyanine field, can be transferred with some confidence to the triazaporphines, subject only to the change in symmetry. These species do have some important properties, however, which make them very useful in the pursuit of molecular electronic applications, namely:

- i) organic solvent soluble, single isomer, species can readily be synthesized.
- ii) Langmuir-Blodgett films may readily be made from amphiphilic species constructed with long alkyl chains (26-28).
- iii) the facile ability to modify the functional group attached to the methine linkage, should provide for the synthesis of a wide range of strategically designed molecules.

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Figure Legends

Figure 1a: Cyclic voltammogram for t-NTNTAP(C₁₅)H₂, (14), in DCB (0.15M TBAP, Pt working electrode, scan rate 100 mV/s).

Figure 1b: Rotating disc electrode (RDE) study for t-NTNTAP(C₁₅)H₂, (14), in DCB (0.15 M TBAP, Pt disc working electrode, scan rate 10 mV/s, 400 rpm, [t-NTNTAP(C₁₅)H₂] = 2x10⁻⁴M).

Figure 2: Differential pulse voltammogram for TBTAP(C₉)H₂ in DCB (0.15 M TBAP, Pt electrode). a: 1.8x10⁻⁵ M; b: 6.1x10⁻⁵ M; c: 7.9x10⁻⁵ M; d: 1.8x10⁻⁴ M. Scan rate 2 mV/s, pulse amplitude 25 mV.

Figure 3: Cyclic voltammogram for TBTAP(C₉)Mg in DMF (0.15 M TBAP, Pt working electrode, scan rate 100 mV/s

Figure 4: Differential pulse voltammogram for TBTAP(C₉)Mg in DMF (0.15 M TBAP, Pt electrode). Scan rate 2 mV/s, pulse amplitude 25 mV.

Figure 5: Absorption spectra of TBTAP(-2)(C₉)H₂ (5) (solid line) in DCB and TBTAP(C₉)Mg (4) (dotted line) in DMF.

Figure 6: Spectroscopic changes accompanying the controlled potential oxidation of TBTAP(-2)(C₉)Mg (4) (8.6 x 10⁻⁴ M) in DMF (0.15 M TBAP). The first (top) spectrum is the starting material, unpolarised. Successive spectra are equilibrium spectra obtained with the electrode polarised at 0.45, 0.50, 0.55 and 0.575 V vs AgCl/Ag.

Figure 7: Spectroscopic changes accompanying the controlled potential oxidation of TBuTBTAP(-2)(C₁₅)H₂ (13) (2.7×10^{-4} M) in DCB (0.15 M TBAP). The first (top) spectrum is the starting material, unpolarised. Successive spectra are equilibrium spectra obtained with the electrode polarised at 0.575, 0.60, 0.625, 0.65, 0.675 and 0.70 V vs AgCl/Ag. (see Experimental section for additional comment).

Figure 8: Spectroscopic changes accompanying the controlled potential reduction of TBuTBTAP(-2)(C₁₅)H₂ (13) (3.8×10^{-4} M) in DCB (0.15 M TBAP). The first (top) spectrum is the starting material, unpolarised. Successive spectra are equilibrium spectra obtained with the electrode polarised at -1.25, -1.275 and -1.30 V vs AgCl/Ag.

Figure 9: Spectroscopic changes accompanying the controlled potential reduction of [TBTAP(-3)(C₉)H₂]⁻ (5⁻) (8.8×10^{-5} M) in DCB (0.15 M TBAP). These spectra were obtained as a series by polarising the electrode from -1.30 to -1.45 V vs AgCl/Ag in 0.025 V steps (see Experimental section for further comment).

Table I: Half-wave Potentials (V vs. Fc/Fc⁺) of Metal-free and Metallated TBTAP(C_n) species

		I	II	II'	III	IV ^a
TBTAP(C ₉)H ₂ ^b (5)	i) ^c	0.79(ir)	0.41	0.24	-1.42	-1.78
	ii)		0.76	0.33	-1.41	-1.86
TBTAP(C ₁₇)H ₂ ^b (11)	i)	0.88(ir)	0.47	0.28	-1.36	-1.72
	ii)		0.84	0.34	-1.37	-1.74
t-BuTBTAP(C ₁₅)H ₂ ^b (13)	i)	0.74(ir)	0.32	0.11	-1.49	-1.88
	ii)		0.71	0.24	-1.51	-1.91
t-NTNTAP(C ₁₅)H ₂ ^b (14)	i)	0.51	0.05	-0.21	-1.48	-1.78
	ii)		0.46	0.01	-1.44	-1.75
TBTAP(C ₉)Mg ^d (4)	i)	0.64(ir)	0.14		-1.50	-2.03
	ii)		0.58	0.12	-1.49	-2.03
TBTAP(C ₁₇)Mg ^d (10)	i)	0.64(ir)	0.14		-1.48	-2.04
	ii)		0.58	0.09	-1.48	-2.02

a) see text for assignments. Potentials cited for irreversible processes, are peak potentials. b) DCB, 0.15 M TBAP. c) i) cyclic voltammetry at 100 mV/s, ii) differential pulse voltammetry at 2 mV/s, pulse amplitude 25 mV. c) DMF, 0.15 M TBAP

Table II. Observed Maxima in the Absorption Spectra of TBTAP(-2)(C_n) Species^a

Complex	λ _{max} (nm) (log ε)				
TBTAP(C ₉)H ₂ (5) ^b	687(4.81)	647(4.62)	621(4.21)	593(4.02)	388(4.48)
TBTAP(C ₁₇)H ₂ (11) ^b	686(4.69)	647(4.49)	619(4.11)	593(3.90)	386(4.49)
TBTAP(C ₉)Mg (4) ^c	672(5.13)	648(4.95)	619(4.28)	595(4.26)	399(4.73)
				355(4.48)	327(4.42)
TBuTBTAP(C ₁₅)H ₂ (13) ^b	693(5.19)	653(4.99)	625(4.62)	598(4.42)	390(4.87)
t-NTNTAP(C ₁₅)H ₂ (14) ^b	785(5.31)	753(5.10)	718(4.63)	683(4.56)	376(4.80)
TBTAP(C ₁₇)Mg (10) ^c	672(5.26)	648(5.05)	617(4.35)	595(4.32)	398(4.80)
				353(4.53)	327(4.46)

a) The solvent was that used for the electrochemistry experiments and therefore contains 0.15 M TBAP. b) solvent, DCB. c) solvent, DMF.

Table III. Observed Maxima in the Absorption of [TBTAP(-1)(C_n)]⁺ Cations^a

Complex	$\lambda_{\text{max}}(\text{nm})$					
TBTAP(C ₉)H ₂ (5) ^b	1019	859	684	570	472	345
TBTAP(C ₉)Mg (4) ^{c,d}	1023	800	678	530	449	330
TBuTBTAP(C ₁₅)H ₂ (13) ^b	1070	856	683	558	470	342

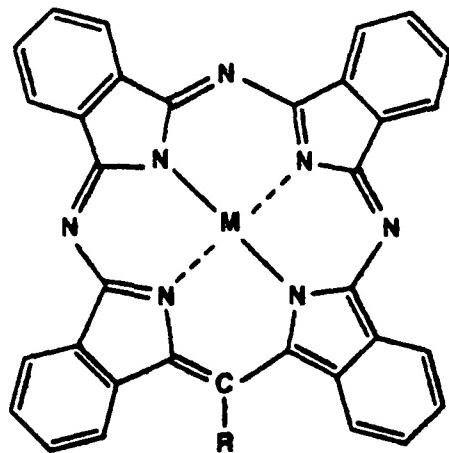
a) The solvent was that used for the electrochemistry experiments and therefore contains 0.15 M TBAP. The product is an equilibrium mixture of mononuclear and binuclear species; the extinction coefficients have therefore not been included. b) DCB c) DMF. d) Incomplete oxidation of parent species.

Table IV. Observed Maxima in the Absorption Spectra of TBTAP(C_n) Anion Radicals

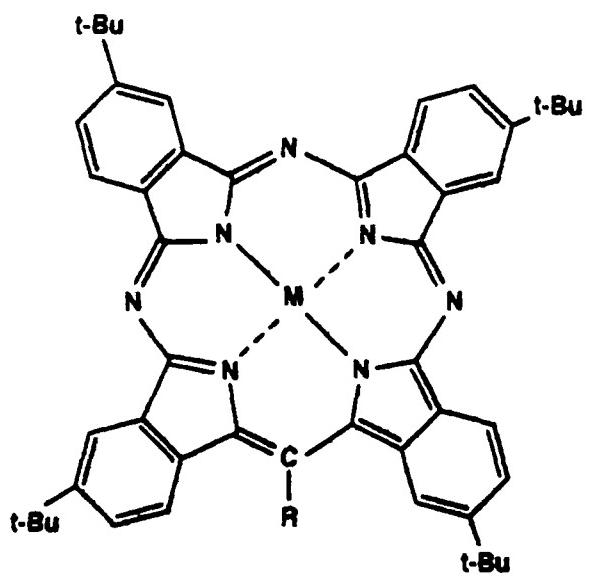
Complex	$\lambda_{\text{max}}(\text{nm}) (\log')$			
[TBTAP(-3)(C ₉)H ₂] ⁻ (5 ⁻) ^b	948(4.38)	864(4.08)	630(4.90)	583(sh)
		442(4.83)	404(4.61)	351(4.61)
[TBTAP(-4)(C ₉)H ₂] ²⁻ (5 ²⁻) ^b		619(sh)	530(4.96)	338(4.55)
[TBTAP(-3)(C ₉)Mg] ⁻ (4 ⁻) ^c	860(4.23)	754(3.89)	631(4.77)	534(sh)
	449(4.78)	401(4.46)	372(4.48)	319(4.41)
[TBuTBTAP(-3)(C ₁₅)H ₂] ⁻ (13 ⁻) ^b	943(4.51)	862(4.27)	630(5.06)	579(sh)
	443(4.96)	403(4.77)	348(4.81)	
[TBuTBTAP(-4)(C ₁₅)H ₂] ²⁻ (13 ²⁻) ^b	623(sh)	528(5.16)	340(4.74)	

a) The solvent was that used for the electrochemistry experiments and contains 0.15 M TBAP.

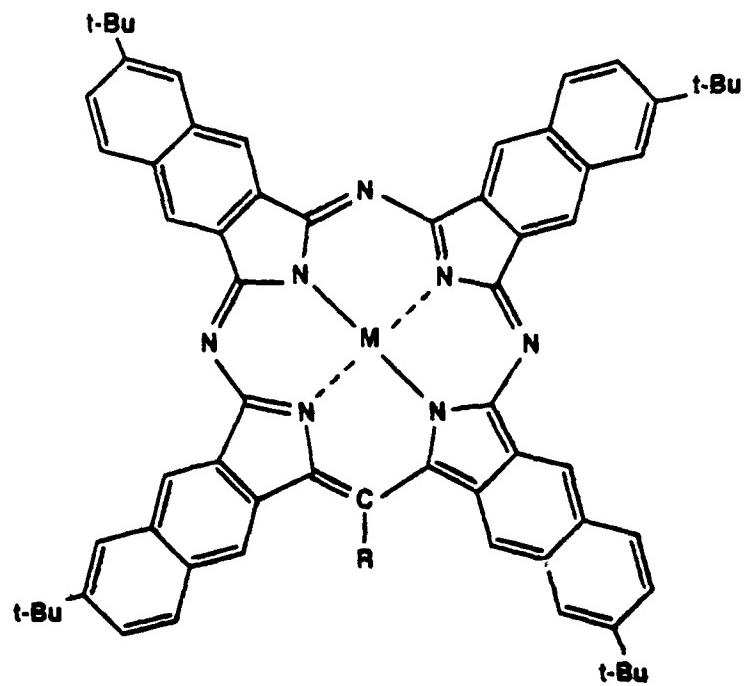
b) DCB. c) DMF.



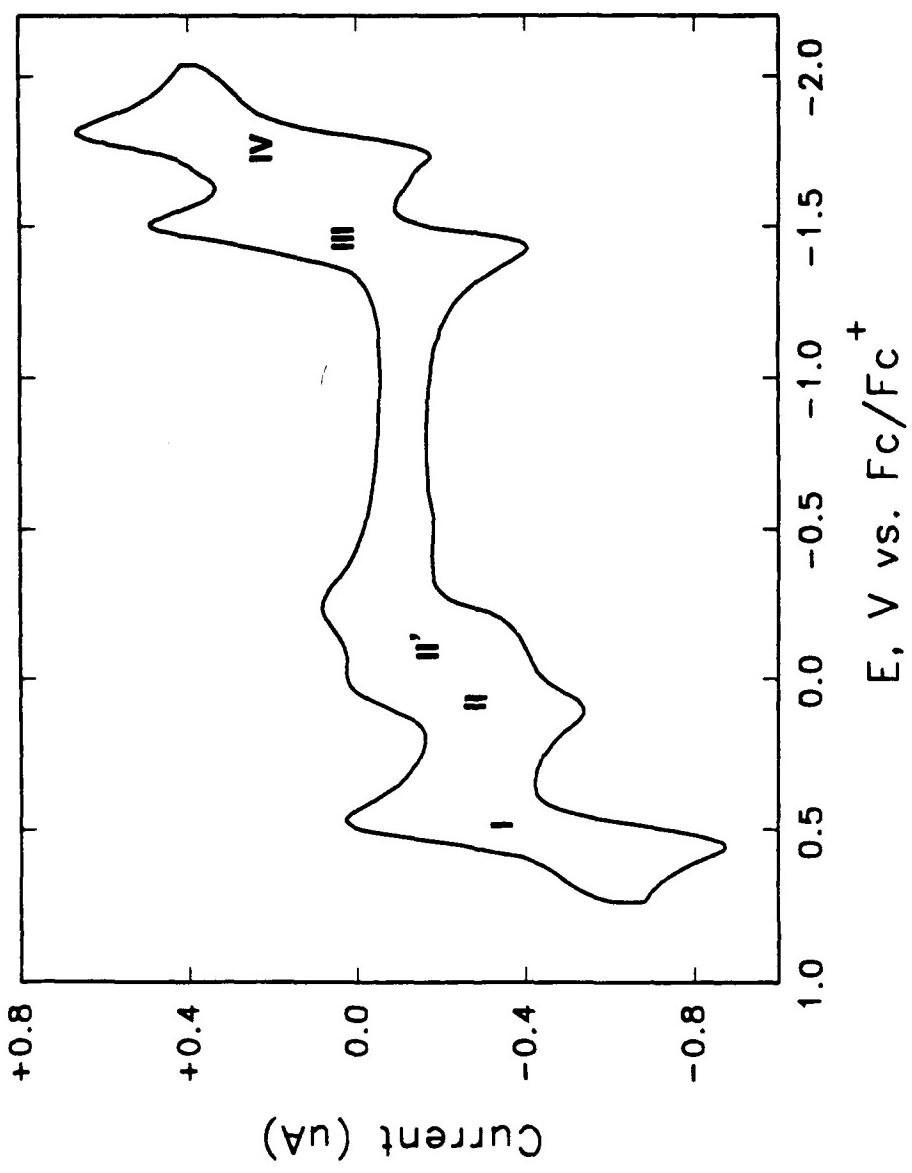
- 1 $M = Mg$, $R = (CH_2)_4CH_3$
- 2 $M = H_2$, $R = (CH_2)_4CH_3$
- 3 $M = Zn$, $R = (CH_2)_4CH_3$
- 4 $M = Mg$, $R = (CH_2)_8CH_3$
- 5 $M = H_2$, $R = (CH_2)_8CH_3$
- 6 $M = Zn$, $R = (CH_2)_8CH_3$
- 7 $M = Mg$, $R = (CH_2)_{12}CH_3$
- 8 $M = H_2$, $R = (CH_2)_{12}CH_3$
- 9 $M = Zn$, $R = (CH_2)_{12}CH_3$
- 10 $M = Mg$, $R = (CH_2)_{16}CH_3$
- 11 $M = H_2$, $R = (CH_2)_{16}CH_3$
- 12 $M = Zn$, $R = (CH_2)_{16}CH_3$

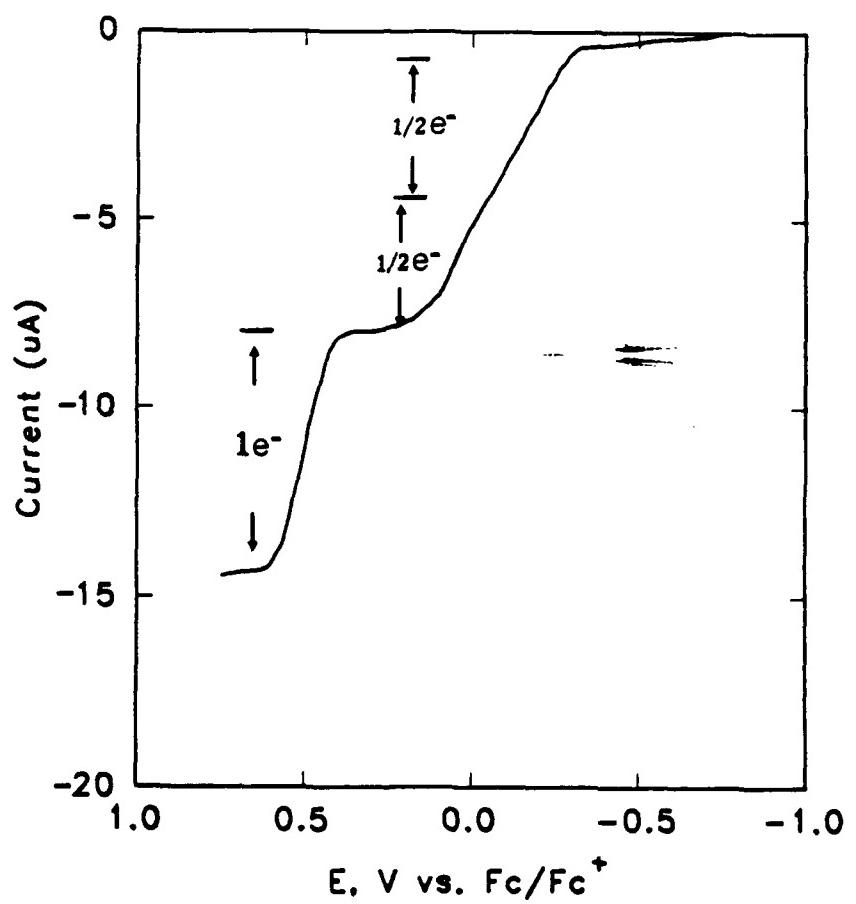


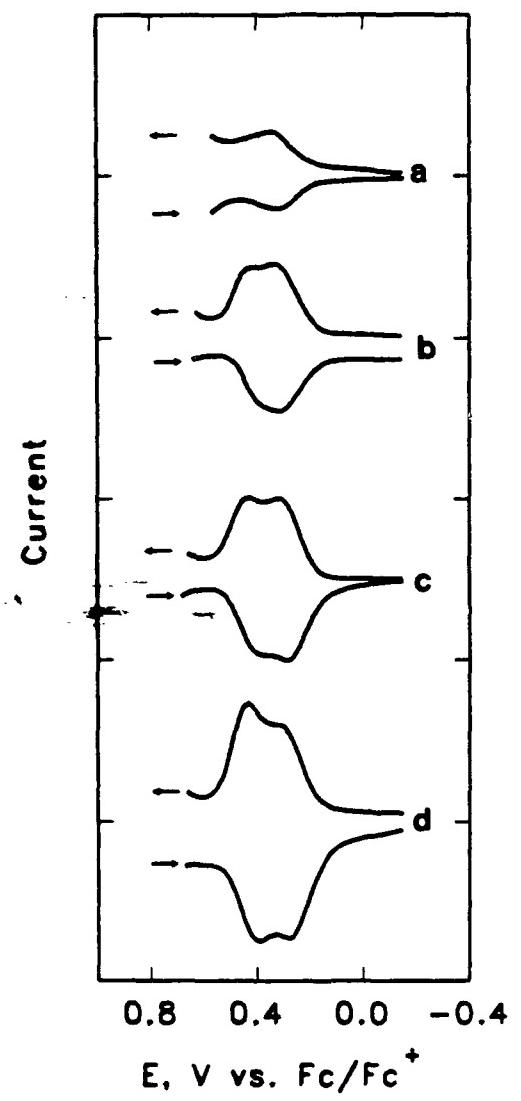
13 M = H₂, R = (CH₂)₁₄CH₃

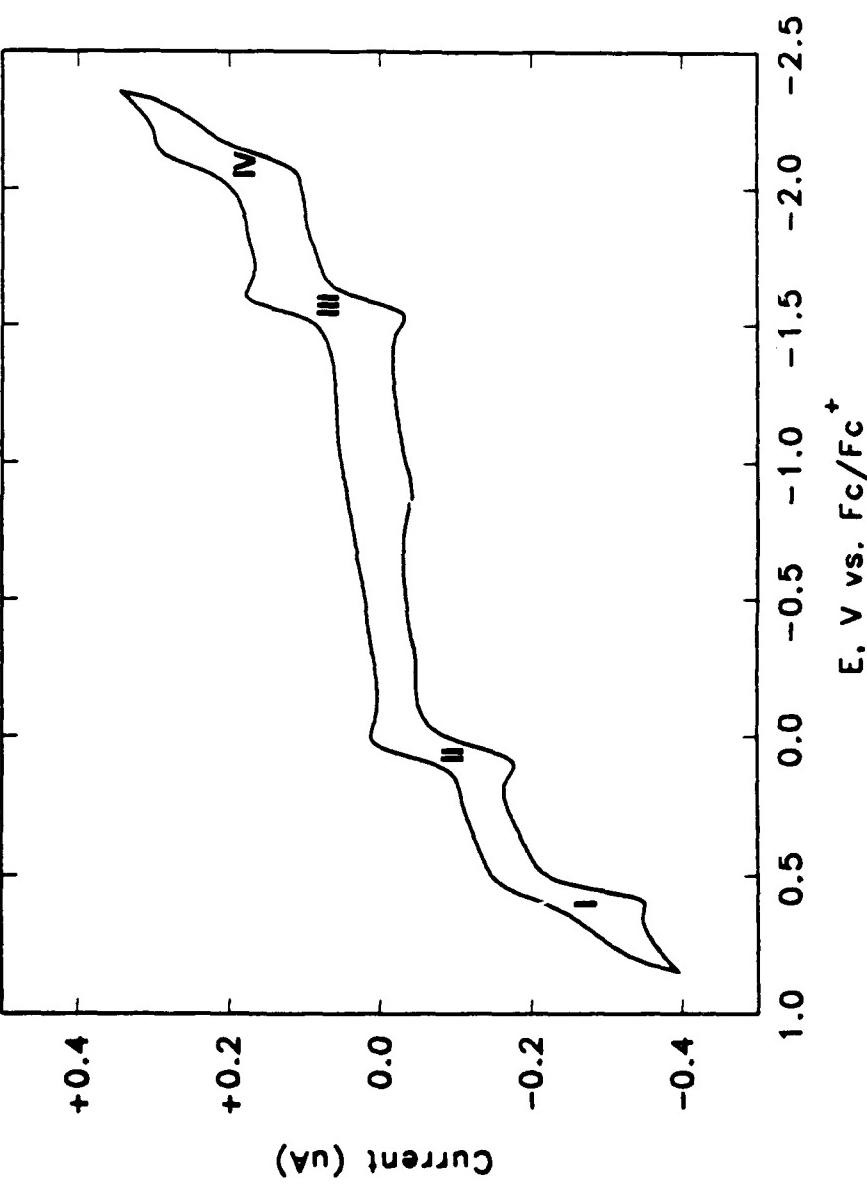


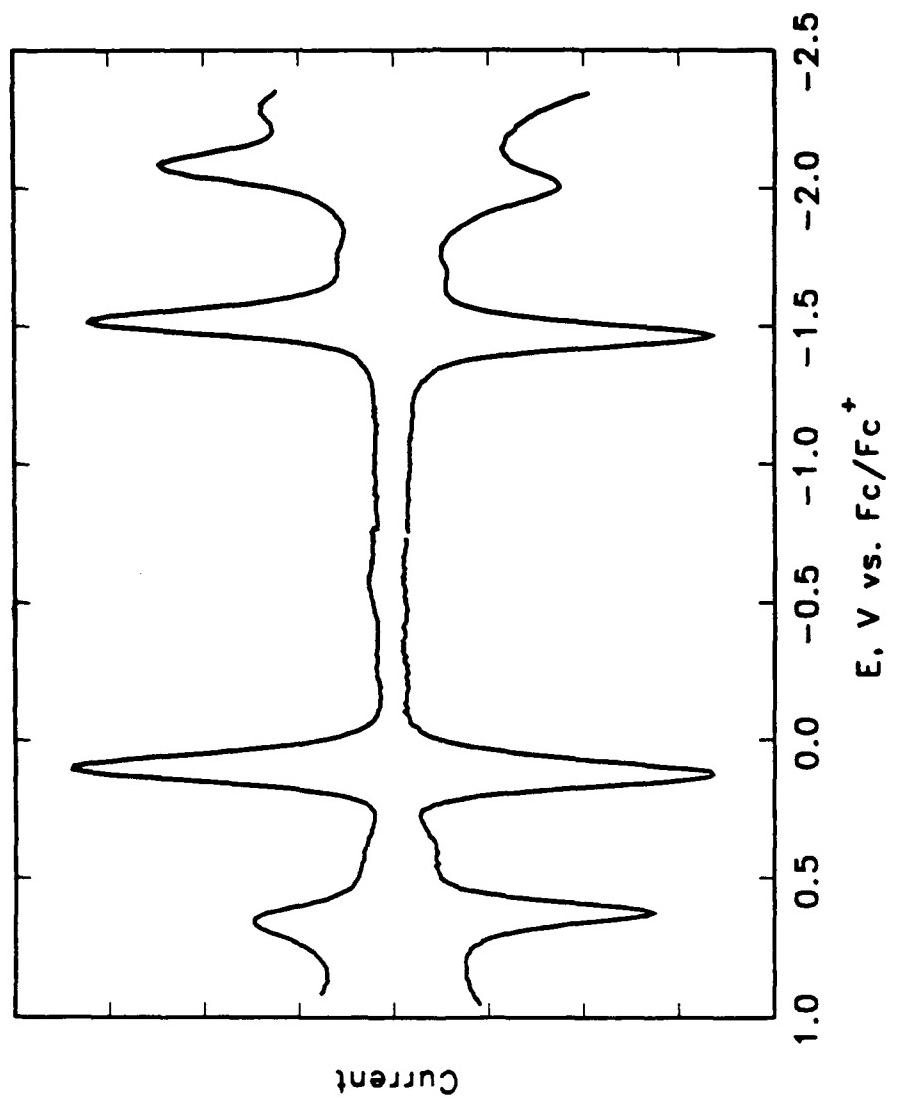
14 $M = H_2$, $R = (CH_2)_{14}CH_3$



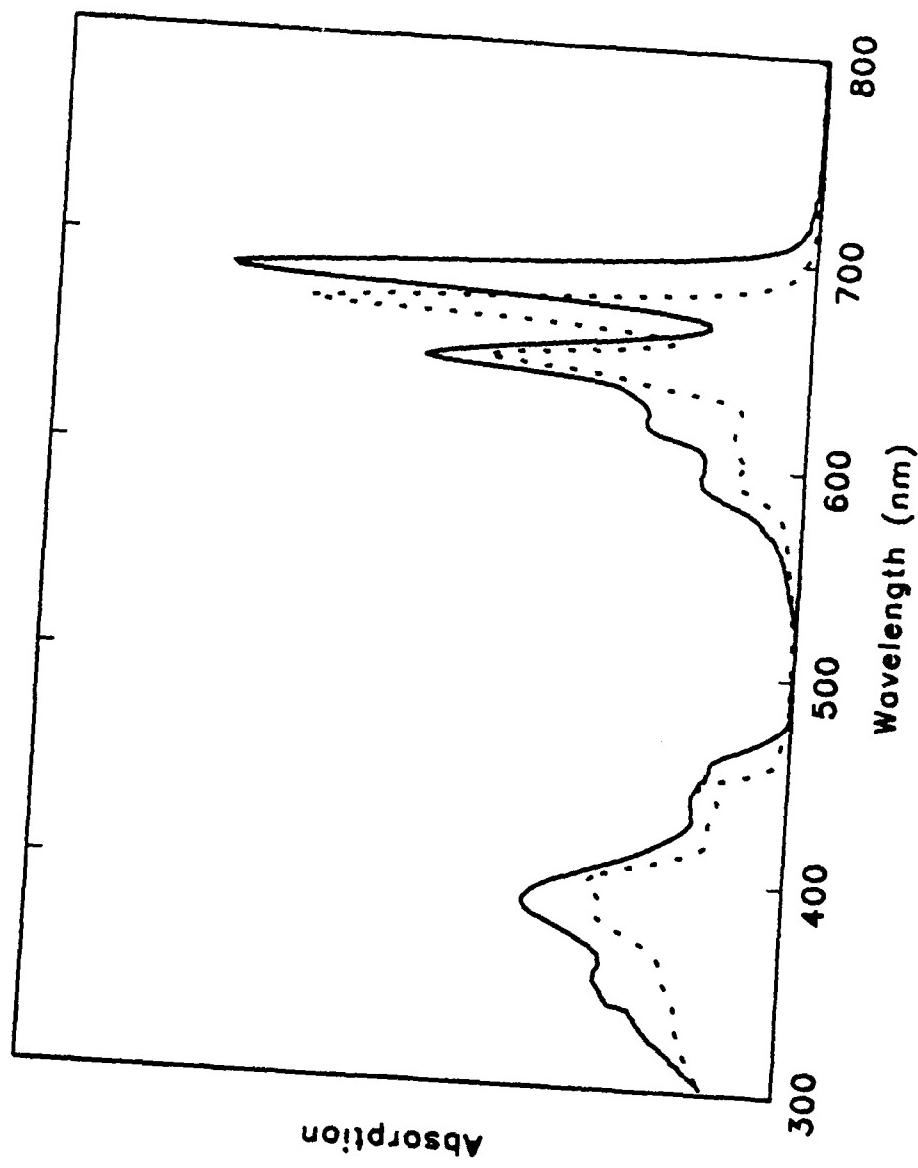


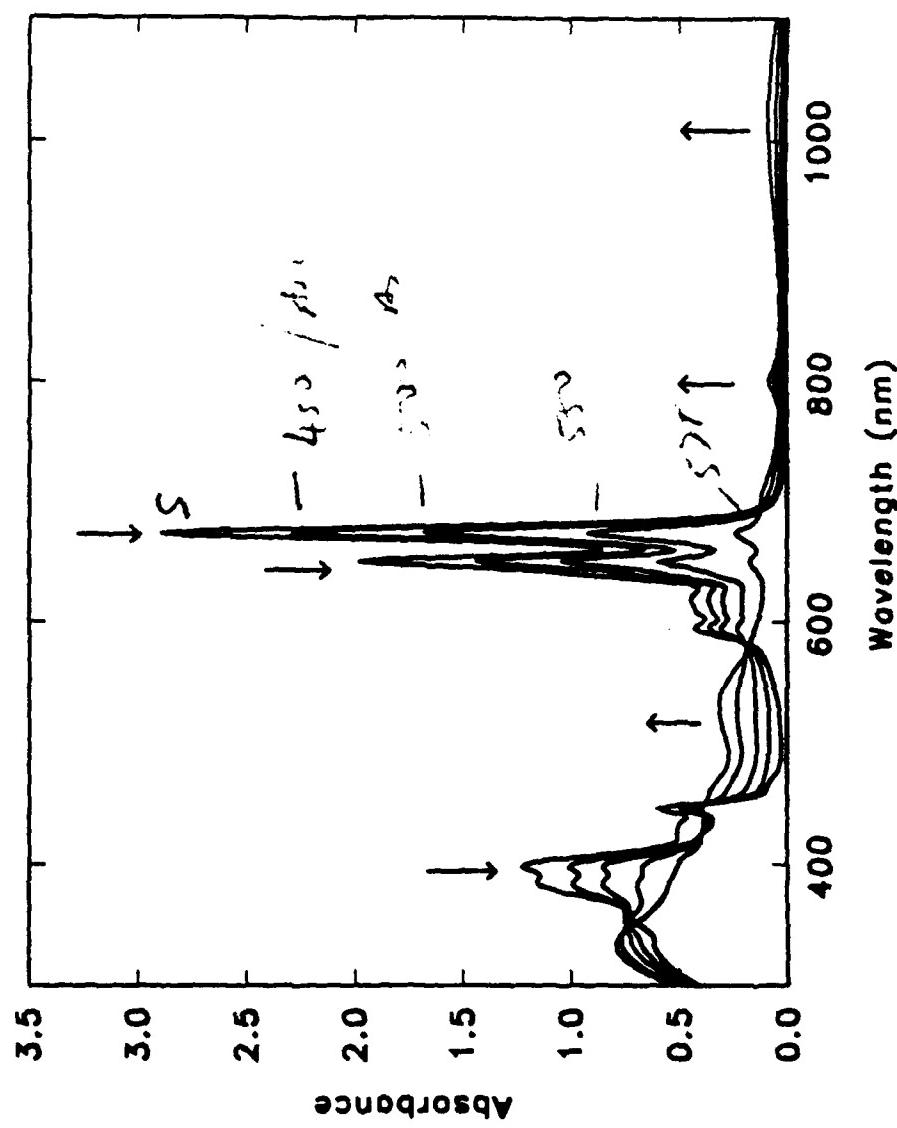


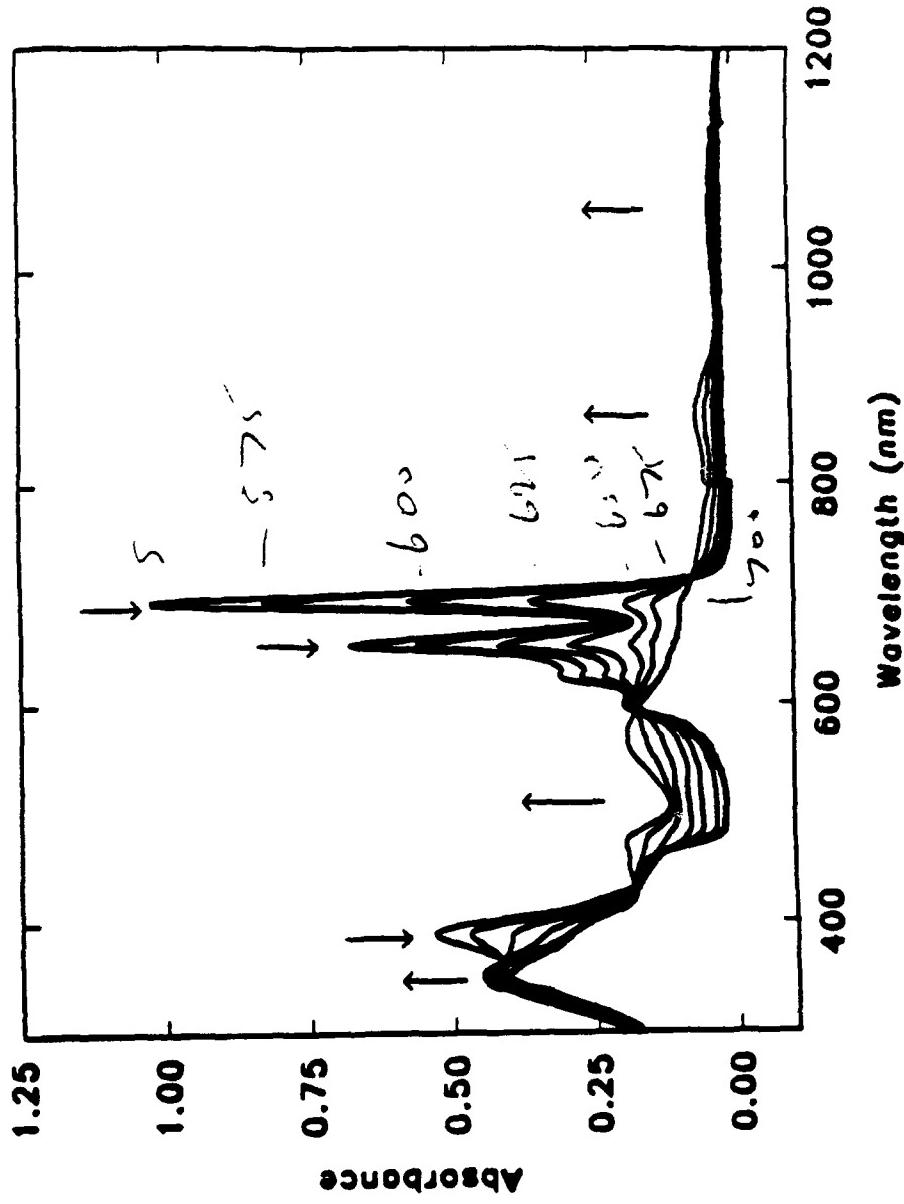




F5







Δ_1 / μ_1 